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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
— *of inventorship (Rule 4.17(iv))*

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(54) **Title:** ETHYL 2-BROMO-4-[2-(3-HALOPYRIDIN-2-YL)-HYDRAZINYL]-4-OXOBUTANOATE HBR SALT, METHOD OF PREPARATION AND USE THEREOF

(57) **Abstract:** Present invention provides novel Ethyl 2-bromo-4-[2-(3-halopyridin-2-yl)-hydrazinyl]-4-oxobutanoate HBr salt, method of preparation and use thereof. The compound is prepared by reaction of ethyl (2Z)-4-[2-(3-chloropyridin-2-yl) hydrazinyl]-4-oxobut-2-enoate with HBr. Invented compound can be used in the preparation of ethyl 2-(3-halopyridin-2-yl)-5-oxopyrazolidine-3-carboxylate which is an intermediate for preparation of pesticides.

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Ethyl 2-bromo-4-[2-(3-halopyridin-2-yl)-hydrazinyl]-4-oxobutanoate HBr salt, method of preparation and use thereof

FIELD OF INVENTION

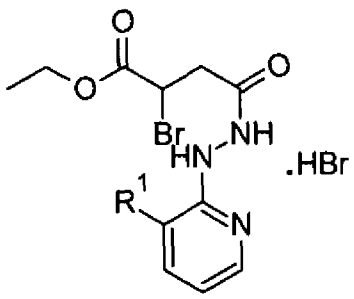
This invention relates to ethyl 2-bromo-4-[2-(3-halopyridin-2-yl)-hydrazinyl]-4-oxobutanoate HBr salt, method of preparation and use thereof. More particularly, the invention relates to the title compound, preparation thereof from ethyl 4-[2-(3-halopyridin-2-yl)hydrazinyl]-4-oxobut-2-enoate and use of the title compound in preparation of ethyl 2-(3-halopyridin-2-yl)-5-oxopyrazolidine-3-carboxylate, which is a useful intermediate for preparation of pesticides.

BACKGROUND AND PRIOR ART

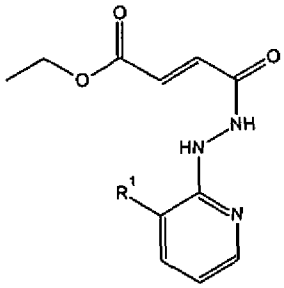
As mentioned above, ethyl 2-(3-halopyridin-2-yl)-5-xopyrazolidine-3-carboxylate (Formula III) is an intermediate for preparation of pesticides.

Present invention discloses Ethyl 2-bromo-4-[2-(3-halopyridin-2-yl)-hydrazinyl]-4-oxobutanoate HBr salt i.e., compound of Formula I, preparation thereof from compound of Formula II and use of compound of Formula I for the preparation of ethyl 2-(3-halopyridin-2-yl)-5-oxopyrazolidine-3-carboxylate i.e., compound of Formula III.

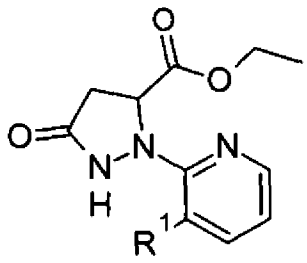
R^1 is a halogen in compounds of Formula I, II & III.



I



II



III

Present invention thus provides a new route for preparation of compound of Formula III, via compound of Formula I which is prepared from compound of Formula II. Compounds of Formula II & III are known compounds. However, preparation of compound of Formula III from the compound of Formula I is not reported in the literature.

OBJECTS OF INVENTION

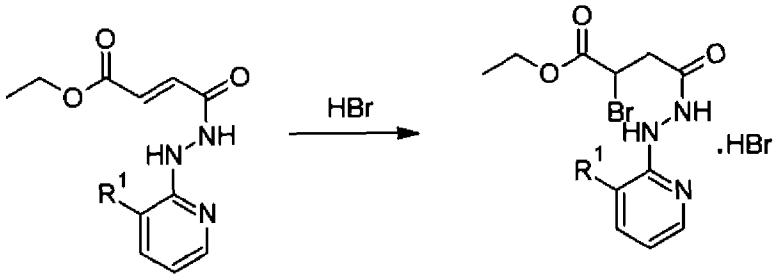
It is an object of invention to provide **compound of Formula I.**

Another object of invention is to provide a **process for preparation of compound of Formula I** from compound of Formula II.

Another object of invention is to provide a **process for preparation of compound of Formula III** (which is an intermediate for preparation of pesticides) from the invented compound of Formula I.

DETAILED DESCRIPTION OF INVENTION

Ethyl 2-bromo-4-[2-(3-halopyridin-2-yl)-hydrazinyl]-4-oxobutanoate HBr salt is prepared by reaction of ethyl 4-[2-(3-halopyridin-2-yl)hydrazinyl]-4-oxobut-2-enoate with HBr as follows:

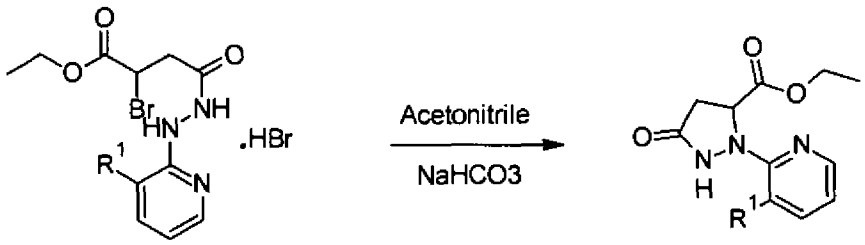


R^1 is a halogen.

The reaction can be carried out from 0-30°C. However, preferred temperature is 8-12°C.

Reaction can be carried out using HBr. It is preferable to use HBr in acetic acid. When HBr in acetic acid is used, excess thereof is removed by distillation under reduced pressure. A solvent in which the desired product does not have significant solubility is added to the reaction mass. The resultant product is filtered and dried.

The invented product thus obtained is taken in a solvent such as acetonitrile and treated with a base such as aqueous $NaHCO_3$ to produce ethyl 2-(3-halopyridin-2-yl)-5-oxopyrazolidine-3-carboxylate as follows:



R^1 is a halogen.

HBr is neutralized and the compound undergoes cyclization as shown in the above reaction. The resultant compound i.e., ethyl 2-(3-halopyridin-2-yl)-5-oxopyrazolidine-3-carboxylate is an intermediate in the preparation of pesticides.

The reagents used in the following examples are for illustration purpose and they are not limitative to the scope of the invention.

Example-1

Preparation of Ethyl 2-bromo-4-[2-(3-chloropyridin-2-yl)-hydrazinyl]-4-oxobutanoate HBr salt:

A 100 ml reaction flask equipped with a magnetic stirrer was charged with 60 ml of 33% HBr in acetic acid. It was cooled to about 5°C. 4.0 gm ethyl 4-[2-(3-chloropyridin-2-yl)hydrazinyl]-4-oxobut-2-enoate was added. The mixture was stirred for 7 hrs. at 8-12°C. Excess HBr in acetic acid was removed by distillation under reduced pressure. 25 ml Ethyl acetate was added to the reaction mass to obtain precipitate which was filtered and dried to get the compound with 94% yield and 85.3% purity.

1H NMR (MeOD, 400 MHz) δ: 8.199-8.177 (dd, J1 = 7.6 Hz, J2 = 1.2 Hz, 1H, pyridyl-H); 7.933-7.914 (dd, J = 6.4 Hz, J2 = 1.2 Hz, 1H, pyridyl-H); 7.076 - 7.041 (dd, J = 7.6 Hz, J2 = 6.4 Hz, 1H, pyridyl-H); 4.61-4.58 (m, 1H, CH-Br), 4.15-4.10 (q, 7.2 Hz, 2H, OCH2); 3.31-3.25 (dd, J = 8.8 Hz, J2 = 6.4 Hz, 1H,); 3.09-3.03 (dd, J = 16.8 Hz, J2 = 6 Hz, 1H,); 1.18 (t, J = 7.2 Hz, 3H, CH3)

m/z = 349 (DI)

IR spectra: 3303.92 cm^{-1}-NH amide stretch, 3119.34 cm^{-1} = -NH stretch, 2935.55 = aromatic -CH stretch, 2746.84 cm^{-1} = aliphatic –CH stretch, 1708.29 cm^{-1} -C=O stretch ester, 1629.51 cm^{-1} -C=O stretch amide, 779.78 cm^{-1} = C-Cl stretch.

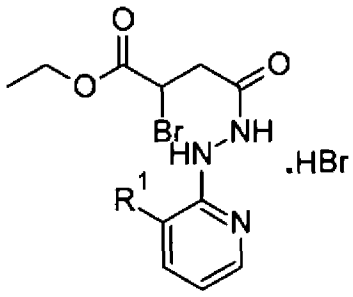
Example-2

Preparation of ethyl 2-(3-chloropyridin-2-yl)-5-oxopyrazolidine-3-carboxylate from compound obtained in Example-1:

100 ml reaction flask was charged with 6.0 gm ethyl 2-bromo-4-[2-(3-chloropyridin-2-yl)hydrazinyl]-4-oxobutanoate HBr salt as obtained in Example-1 and 100 ml acetonitrile. The mixture was cooled to 5°C. 10% NaHCO3 solution was added drop wise with stirring and the temperature was allowed to raise to room temperature during which HBr was neutralized and the compound underwent cyclization. The reaction mixture was washed with brine and the organic layer was separated & dried over anhydrous Na_2SO_4. Solvent was removed by distillation under reduced pressure and the residue was washed with 2.5-5% ethanol in water and dried under reduced pressure to get the product with 84.6% yield and 96% purity.

We Claim:

1. Compound of Formula (I)



(I)

wherein R^1 is a halogen.

2. A process for preparation of compound of Formula (I) as claimed in claim 1 by reaction of ethyl 4-[2-(3-halopyridin-2-yl)hydrazinyl]-4-oxobut-2-enoate with HBr.

3. A process as claimed in claim 2, wherein the reaction is carried out at 0-30°C.

4. A process as claimed in claim 2, wherein HBr is taken in acetic acid, and after completion of the reaction, excess HBr in acetic acid is removed by distillation under reduced pressure.

5. A process as claimed in claim 2, wherein HBr is taken in acetic acid, and after completion of the reaction, excess HBr in acetic acid is removed by distillation under reduced pressure and thereafter the product is separated from reaction mass by adding to the reaction mass a solvent in which the product does not have significant solubility, followed by filtration and drying.

6. A process for preparation of ethyl 2-(3-halo-pyridin-2-yl)-5-oxopyrazolidine-3-carboxylate from the compound of Formula (I) as claimed in claim 1 by neutralization with a base.

7. A process as claimed in claim 6, wherein said base is $NaHCO_3$.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
C07D401/04,C07D231/08,A01N43/56 Version=2019.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

TotalPatent One, IPO Internal Database, STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US8217179B2 SHENYANG SINOCHEM AGROCHEMICALS R&D CO LTD 10 July 2012 (2012-07-10). Column 5, example 1; column 2, summary of the invention.	1-7
Y	EP1417175B1 E I DU PONT DE NEMOURS AND CO 24 July 2013 (2013-07-24). Page 5, lines 5-29, Scheme 1; page 7, paragraph 35.	1-7
Y	EP2100889B1 E I DU PONT DE NEMOURS AND CO 20 April 2011 (2011-04-20). Page 6, Scheme 5.	1-7
Y	EP2093223B1 ISHIHARA SANGYO KAISHA LTD 21 August 2013 (2013-08-21). Page 22, paragraph 150, reaction [Q].	1-7
Y	US8492409B2 SHENYANG SCIENCREAT CHEMICALS CO LTD 23 July 2013 (2013-07-23). Column 20, example 3.2.	1-7

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT
Information on patent family members

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